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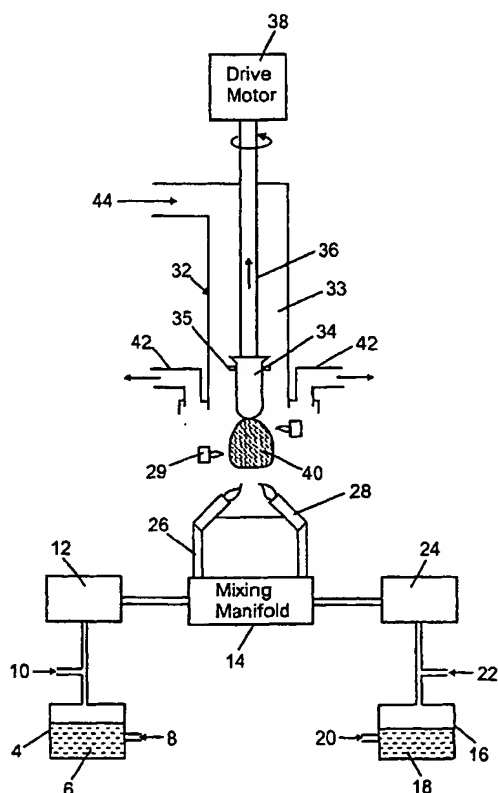
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(54) Title: **METHOD FOR PRODUCING TITANIA-DOPED FUSED SILICA EXTREME ULTRAVIOLET LITHOGRAPHY SUBSTRATES GLASS**

(57) Abstract: A titania precursor (18) and a silica precursor (6) are mixed in a manifold (14) and are fed to a burner (28) to create soot (40) which is deposited on a deposition surface (34) which is rotated and elevated. The end product is useful for Extreme UV lithography.



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METHOD FOR PRODUCING TITANIA-DOPED FUSED SILICA EXTREME ULTRAVIOLET LITHOGRAPHY SUBSTRATES GLASS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention relates generally to a method for forming an EUV(Extreme UltraViolet) lithography glass substrate. More specifically, the invention relates to a method for producing an extreme ultraviolet (EUV) lithography glass titania-doped fused silica substrate and an extreme ultraviolet (EUV) lithography glass titania-doped fused silica glass substrate having low water content.

2. Background Art

Extreme ultraviolet (EUV) lithography is emerging as one of the next-generation lithography techniques that will allow high-volume production of integrated circuits with sub-100-nm features. EUV lithography as currently contemplated involves producing electromagnetic radiation at around 13 nm. The EUV radiation may be produced, for example, using a 1064-nm neodymium-YAG laser which produces a xenon gas plasma or from a synchrotron source. A condenser collects the EUV radiation and projects it onto a mask containing a pattern to be replicated on a silicon wafer. The mask reflects the EUV radiation into an imaging system, which then projects an image onto a resist-coated silicon wafer. The pattern is later transferred to the silicon wafer by etching.

The mask structure consists of a substrate ("mask blank"), a reflective multilayer stack formed on the mask blank, and an absorber formed on the multilayer stack. Typically, the multilayer stack includes alternating layers of Mo and Si or Mo and Be. The absorber defines the pattern to be replicated on the silicon wafer. The mask blank may be made of silicon or glass or other suitable material. It is important that the mask blank has a low thermal expansion so that it does not distort under exposure to the EUV radiation. Titania-doped fused silica ($\text{SiO}_2\text{-TiO}_2$) is a preferred glass that can be made to have a very low thermal expansion, *i.e.*, lower than pure fused silica with the potential for a coefficient of thermal expansion that approximates

zero. The coefficient of thermal expansion of the $\text{SiO}_2\text{-TiO}_2$ glass can be controlled by adjusting the percent weight content of TiO_2 in the glass.

Commercial processes for producing $\text{SiO}_2\text{-TiO}_2$ glass involve transporting a mixture of a silica precursor and a titania precursor to a reaction site, thermally
5 decomposing the mixture of precursors (usually via flame hydrolysis) into $\text{SiO}_2\text{-TiO}_2$ particles ("soot"), and depositing the soot on a support. In the conventional boule process, the soot is captured in a cup of a refractory furnace at consolidation temperatures (typically 1200 to 1900°C) so as to allow the soot to immediately consolidate into a solid body ("boule"). These high consolidation temperatures may
10 result in compositional variations within the glass, which would result in the glass having non-uniform thermal expansion properties. Therefore, a production method which favors homogeneity in the $\text{SiO}_2\text{-TiO}_2$ glass is desirable.

For environmental reasons, commercial processes for producing $\text{SiO}_2\text{-TiO}_2$ glass use a chloride-free material such as octamethylcyclotetrasiloxane (OMCTS), a
15 siloxane, as a silica precursor. Usage of organic precursors and a hydrogen-containing fuel for thermal decomposition of the organic precursors inherently results in the $\text{SiO}_2\text{-TiO}_2$ glass containing more OH (often referred to as water) than can be tolerated by infrared transmission applications or deep-UV applications such as at 157 nm. In particular, OH has some absorption at these wavelengths. Therefore, a
20 production method which favors dehydration of the $\text{SiO}_2\text{-TiO}_2$ glass is also desirable.

SUMMARY OF THE INVENTION

In one aspect, the invention relates to a method for producing a EUV
lithography glass substrate. The method comprises synthesizing particles of silica and
25 titania by delivering a mixture of a silica precursor and a titania precursor to a burner, growing a porous preform by successively depositing the particles on a deposition surface while rotating and translating the deposition surface relative to the burner, consolidating the porous preform into a dense glass.

Other aspects and advantages of the invention will be apparent from the
30 following description and the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic of a system for producing SiO₂-TiO₂ EUV lithography glass in accordance with an embodiment of the invention.

5 Figure 2 is a top view of an EUV lithography mask blank.

Figure 3 is a side view of the EUV lithography mask blank shown in Figure 2.

DETAILED DESCRIPTION OF THE INVENTION

The invention includes making thermally stable EUV lithography glass
10 substrates such as optical mirror element and mask substrates. PCT patent
publication WO0108163 A1, EUV SOFT X-RAY PROJECTION
LITHOGRAPHIC METHOD SYSTEM AND LITHOGRAPHY ELEMENTS
of CORNING INCORPORATED by Davis et al. (Application No. US0018798
US, Filed 20000710, A1 Published 20010201) and WO0107967 A1, EUV
15 SOFT X-RAY PROJECTION LITHOGRAPHIC METHOD AND MASK
DEVICES of CORNING INCORPORATED by Davis et al. (Application No.
US0019060 US, Filed 20000713, A1 Published 20010201) which are hereby
incorporated by reference shows EUV lithography mirror element and mask
substrates. Embodiments of the invention provide a method for producing EUV
20 lithography SiO₂-TiO₂ glass substrates with low variations in CTE within the
substrate, preferably with the EUV lithography substrate having a very low variation
in coefficient of thermal expansion (CTE) within the substrate, preferably a
homogeneous CTE with a variation of 0 ± 5 ppb/°C. The method involves
transporting silica and titania precursors in vapor form to deposition burners. The
25 precursors exit the deposition burners where they react to form fine SiO₂-TiO₂
particles ("soot"). The soot collect on a deposition surface to form a porous preform.
The method further includes consolidating the porous preform to give a dense EUV
lithography SiO₂-TiO₂ glass in a separate step. Consolidating the glass in a separate
step eliminates the need to capture the soot at consolidation temperatures. This allows

the soot to be deposited at lower temperatures (typically, 200°C to 500°C lower) than possible with the conventional boule process. SiO₂-TiO₂ glass having low OH content can be produced by exposing the preform to a dehydrating agent, such as chlorine or fluorine, prior to consolidation. Chlorine and/or fluorine treatment would also remove impurities from the glass which could result in seeds.

In one embodiment of the invention, production of EUV lithography SiO₂-TiO₂ glass utilizes a vapor-axial deposition (VAD) process with two delivery systems used to provide entrained vapors of titania precursor and silica precursor. The two separate vapor trains feed into a manifold where they are mixed together. The mixture is then carried through fume lines to deposition burners where it reacts to form soot. The soot is deposited on a bait which is rotated and moved axially within an enclosure. The porous preform formed by the soot is thermally consolidated into dense glass in a later separate step. An intermediate chlorine and/or fluorine treatment step may be used to remove impurities or adsorbed water from the glass. Relatively large and homogeneous SiO₂-TiO₂ EUV lithography glass substrates, *e.g.*, 6" x 6" x 0.25" substrates and larger, can be made using this process.

Figure 2 is a schematic of a system, generally designated by the numeral 2, for use in practicing the present invention. The system 2 includes source 4 of a silica precursor 6. There are many choices available for the silica precursor, *e.g.*, a siloxane such as OMCTS (Si₄O₄(CH₃)₈), halogen-based precursors such as silicon tetrachloride (SiCl₄), silane (SiH₄), and other silicon-containing compounds. In general, halogen-free precursors are preferred because they are more environmentally friendly. Silane exists in vapor form at room temperature and does not need a vaporization step prior to mixing with the titania precursor. The silica precursor 6 is pumped into the source 4 at a predetermined rate. The source 4, which may be a vaporizer or evaporator tank or similar equipment, converts the silica precursor 6 into vapor form if the silica precursor 6 is not already in vapor form. An inert carrier gas 8, *e.g.*, nitrogen, carries the silica precursor 6 vapors through a distribution system 12 to a manifold 14. A stream of inert gas 10, *e.g.*, nitrogen, is brought into contact with the silica precursor 6 vapors to prevent saturation.

The system 2 further includes a source 16 of the titania precursor 18, *e.g.*, a titanium alkoxide such as titanium isopropoxide (Ti(OPri)₄). The titania precursor 18

is pumped into the source 16 at a predetermined rate. The source 16 converts the titania precursor 18 into vapor form if the titania precursor 18 is not already in vapor form. A stream of inert gas 22, *e.g.*, nitrogen, can be brought into contact with the vaporous titania precursor to prevent saturation of the vapors. An inert carrier gas 20, *e.g.*, nitrogen, entrains the titania precursor 18 vapors and carries the vapors through a distribution system 24 to manifold 14, where they are mixed with the silica precursor 6 vapors. The mixture of vaporous precursors passes through heated fume lines 26 to deposition burners 28 positioned below a multi-chambered hood 32. The temperatures of the fume lines 26 are preferably controlled to prevent reaction prior to reaching the deposition burners 28.

Prior to injecting the mixture into the deposition burners 28, a bait 34 is disposed in the center chamber 33 of the multi-chambered hood 32. Typically, the bait 34 is made of fused quartz. However, the bait 34 may also be made of other bait materials such as alumina or graphite. Further, the bait 34 may be shaped like a rod, as shown in the drawing, or may have other desired shape. For example, the bait 34 may be shaped like a ball or a plate. The upper end of the bait 34 is connected to a spindle 36, for example, by pin 35. The spindle 36 is in turn connected to a drive motor 38. When the drive motor 38 is energized, the spindle 36 and the bait 34 rotate in unison and ascend within the chamber 33 at predetermined speeds. The speed at which the bait 34 ascends is critical to the temperature profile and shape of the porous preform 40 formed on the bait 34. A typical bait speed is 0.3 to 0.5 mm/min.

Burner placement is fixed and bait speed is adjusted to maintain a constant burner-to-soot preform distance during deposition. Although two deposition burners 28 are shown, it should be clear that one or more than two deposition burners can be used. In general, the number of deposition burners will depend on the size of porous preform to be made. The deposition burners 28 are typically inclined at an angle with respect to the translation axis of the bait 34. Auxiliary heat burners 29 may also be provided to promote the thermal environment needed to form the $\text{SiO}_2\text{-TiO}_2$ particles. Improper placements of the deposition burners 28 and the auxiliary heat burners 29 could result in both excessively hot and cold regions on the preform. The occurrence of these will cause unwanted effects on the density, shape, deposition efficiencies, and other related defects of the preform.

The mixture of vaporous precursors are injected into the deposition burners 28, as previously described. The vaporous precursors exit the deposition burners 28 where they react to form $\text{SiO}_2\text{-TiO}_2$ soot. The soot is formed by hydrolysis or thermal oxidation reaction of the precursors with a methane-oxygen flame. Alternatively, an oxyhydrogen flame could be used to form the soot. The soot is deposited on the lower end of the bait 34 to form a columnar porous preform 40. The lower end of the bait 34 on which the preform is formed is generally spherical in shape but could be planar or have other shape. The preform 40 grows as more soot is deposited and the bait 34 ascends. Spurious soot is generated at the time of deposition and is removed through the exhaust chambers 42. The chamber 33 in which the spindle 36 and bait 34 travel is provided with a stream of clean air 44 that is directed towards the emerging preform 40. This stream of air 44 directs the spurious soot outward and away from the preform 40 into the exhaust chambers 42 which carry it away. This is a critical step in the reduction of physical defects on the preform 40.

After the preform 40 is formed, the process is shut-down and the preform 40 is removed to an environmentally controlled storage area (not shown) where it will await consolidation process and, if needed, an intermediate chlorine treatment step. The consolidation of the porous preform 40 into a dense EUV lithography glass involves heating the preform to consolidation temperatures, typically 1200 to 1900°C with preferred values in a range from 1300 to 1700°C, in vacuum or at atmospheric pressure. Chlorine treatment involves heating the porous preform 40 in chlorine gas, usually in the presence of an inert gas such as helium. Chlorine treatment is generally best at temperatures just prior to consolidation of the preform 40, typically 900 to 1100°C. The high temperatures allow reaction of metal impurities to form volatile metal chlorides which are removed. Additionally, the chlorine removes OH from the glass structure. Dehydration of the porous preform prior to consolidation can also be accomplished by exposing the porous preform to a fluorinating gas, such as CF_4 or SiF_4 , usually in the presence of an inert gas such as helium.

Preferably the low thermal expansion EUV lithography $\text{SiO}_2\text{-TiO}_2$ glass formed by the process above has TiO_2 content in a range from 2 to 12% by weight. The weight percent of TiO_2 in the glass can be adjusted by changing the amount of titanium precursor 18 delivered to the deposition burners 28. The consolidated

preform made by the process above is formed into a finished mask blank for EUV lithography. Forming into a finished EUV lithography mask blank includes cutting the consolidated dense glass preform into a desired shape, polishing the surface of the preform, and cleaning the preform. Figures 2 and 3 show a EUV lithography mask blank 46 having a planar top surface 48 and a planar bottom surface 50. A consolidated preform produced by the process above can be cut as necessary to form the mask blank 46. A mask for EUV lithography can be formed by depositing alternating layers of reflective coating, *i.e.*, Mo/Si or Mo/Be, on the glass substrate and depositing an absorber, *e.g.*, Al or Si, on the multilayer reflective coating.

10 Dry SiO₂-TiO₂ glass can be used in fabricating optical elements for infrared transmission in the 700 to 1600 nm wavelength range, and more specifically in the 1200 to 1600 nm wavelength range. Dry SiO₂-TiO₂ glass can also be used in fabricating optical elements for deep-UV applications such as at 157 nm.

15 While the invention has been described with respect to a limited number of embodiments, those skilled in the art, having benefit of this disclosure, will appreciate that other embodiments can be devised which do not depart from the scope of the invention as disclosed herein. Accordingly, the scope of the invention should be limited only by the attached claims.

What is claimed is:

1. A method for forming an EUV lithography glass substrate comprising:
synthesizing particles of silica and titania by delivering a mixture of a silica precursor and a titania precursor to a burner;
5 growing a porous preform by successively depositing the particles on a deposition surface while rotating and translating the deposition surface relative to the burner; and
consolidating the porous preform into a dense EUV lithography glass and forming the consolidated dense EUV lithography glass into a homogenous EUV
10 lithography glass substrate.
2. The method of claim 1, wherein a translation speed of the deposition surface is adjusted to maintain a substantially constant distance between the porous preform and the burner during deposition.
- 15 3. The method of claim 1, wherein the silica and titania particles are deposited at a temperature below that required to consolidate the porous preform into dense glass.
4. The method of claim 3, wherein consolidating the porous preform into dense
20 glass comprises heating the porous preform to a temperature in a range from 1200 to 1900°C.
5. The method of claim 1, further comprising dehydrating the porous preform by exposing the porous preform to a heated, halide-containing atmosphere prior to
25 consolidation.
6. The method of claim 5, wherein the heated, halide-containing atmosphere comprises chlorine.
- 30 7. The method of claim 5, wherein the heated, halide-containing atmosphere comprises fluorine.

8. The method of claim 5, wherein the temperature of the heated, halide-containing atmosphere is in a range from 900 to 1100°C.

5 9. The method of claim 1, wherein the glass contains 2 to 12% by weight titania.

10. A method for producing an EUV lithography glass substrate having low OH content, comprising:

synthesizing particles of silica and titania by delivering a mixture of a silica
10 precursor and a titania precursor to a burner;
growing a porous preform by successively depositing the particles on a
deposition surface while rotating and translating the deposition surface relative to the
burner;
dehydrating the porous preform by exposing the porous preform to a heated,
15 halide-containing atmosphere; and
consolidating the dehydrated porous preform into a dense EUV lithography
glass and forming the consolidated dense EUV lithography glass into a homogenous
EUV lithography glass substrate.

20 11. The method of claim 10, wherein the heated, halide-containing atmosphere comprises chlorine.

12. The method of claim 10, wherein the heated, halide-containing atmosphere
comprises fluorine.

25

13. The method of claim 10, wherein a translation speed of the deposition surface
is adjusted to maintain a substantially constant distance between the porous preform
and the burner during deposition.

30 14. The method of claim 10, wherein the silica and titania particles are deposited
at a temperature below that required to consolidate the porous preform into dense
glass.

15. The method of claim 14, wherein consolidating the porous preform into dense glass comprises heating the porous preform to a temperature in a range from 1200 to 1900°C.

5 16. A mask blank for extreme ultraviolet lithography made by a process comprising:

synthesizing particles of silica and titania by delivering a mixture of a silica precursor and a titania precursor to a burner;

10 growing a porous preform by successively depositing the particles on a deposition surface while rotating and translating the deposition surface relative to the burner;

consolidating the porous preform into a dense glass; and

finishing the dense glass into a extreme ultraviolet lithography mask blank.

15 17. The mask blank of claim 16, comprising the glass contains 2 to 12% by weight titania.

18. A mask blank for extreme ultraviolet lithography made by a process
20 comprising:

synthesizing particles of silica and titania by delivering a mixture of a silica precursor and a titania precursor to a burner;

25 growing a porous preform by successively depositing the particles on a deposition surface while rotating and translating the deposition surface relative to the burner;

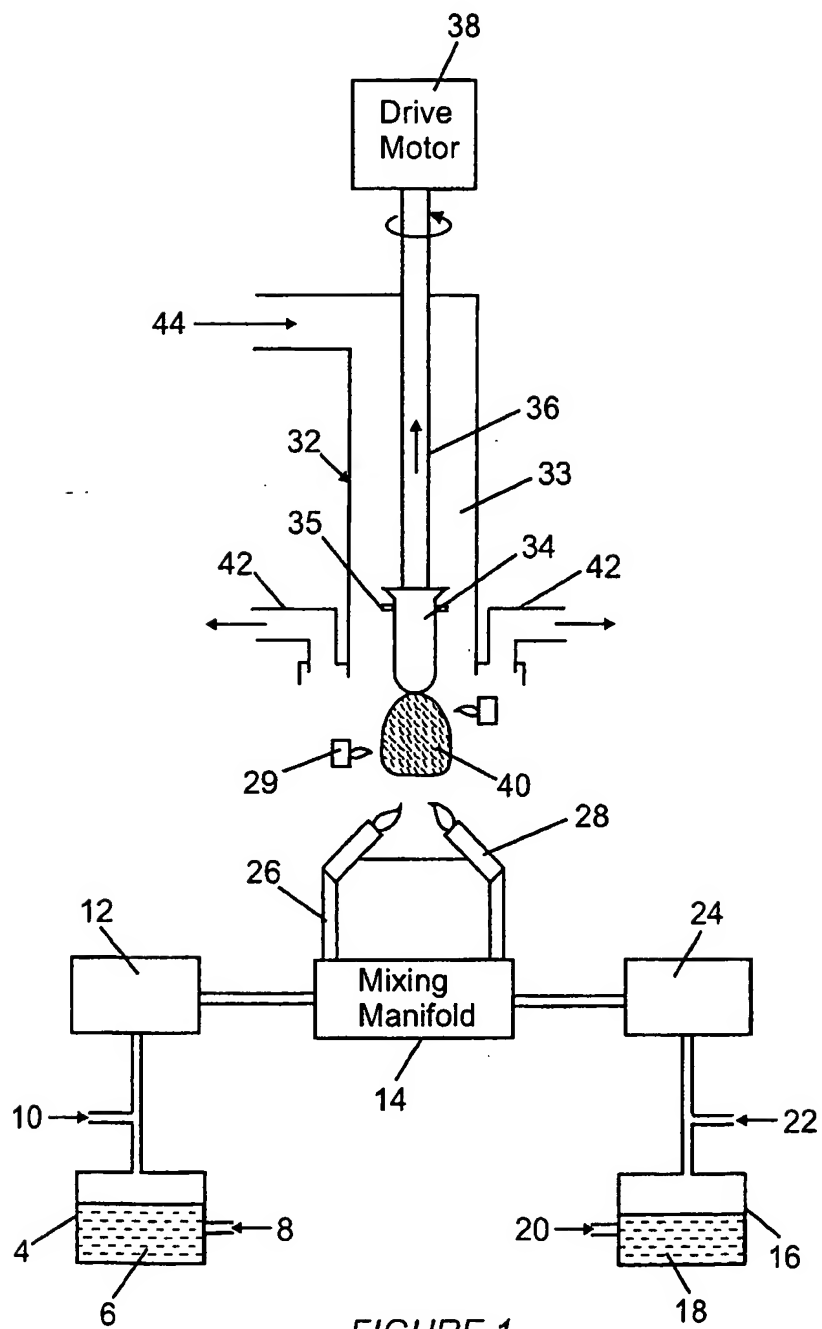
dehydrating the porous preform by exposing the porous preform to a heated, halide-containing atmosphere;

consolidating the porous preform into a dense glass; and

finishing the dense glass into an extreme ultraviolet lithography mask blank.

30 19. The mask blank of claim 18, wherein the glass contains 2 to 12% titania.

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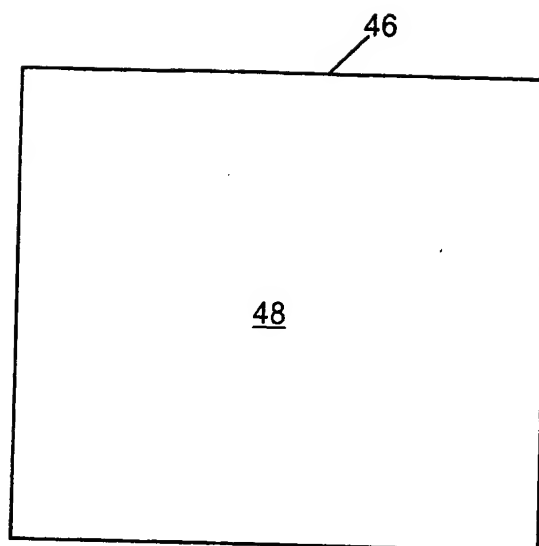


FIGURE 2

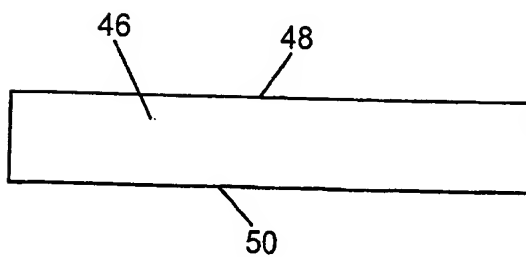


FIGURE 3

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US02/09461

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C03B 8/04
US CL : 65/414, 17.4

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 65/414, 17.4

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
WEST

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 4,440,558 A (NATH et al) 03 April 1984 (03.04.1984), claim 13 and figure 1.	1,3,16,18 ----- 2,4-15, 17, 19

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

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